

June 2, 2004

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Re: NREL Subcontract #ADJ-1-30630-12

Dear Ken:

This report covers research conducted at the Institute of Energy Conversion (IEC) for the period Mar. 09, 2004 to Apr. 09, 2004, under the subject subcontract. The report highlights progress and results obtained under Task 2 (CuInSe₂-based Solar Cells).

Task 2: CuInSe₂-based Solar Cells

In-Line Evaporation

Thermocouples attached to the web shield, and in contact with the web's coating side just before and after the deposition zone are now being used to control both substrate heaters. Thermocouples imbedded into the heaters are used for monitoring the heaters. As a result, different web substrates can be tested without cumbersome calibrating procedures.

The new Cu source that was put in service, as reported earlier, has now been operating satisfactorily for about three months. Utilizing the method of determining the TC offset, described previously, the reproducibility of film composition has been quite acceptable with the Cu/GaIn ratio staying, between 0.83 to 0.93.

During the present period work has been started to improve Se delivery to the substrate both in terms of total rate and effusion geometry. The first issue was to reduce heat load onto the Se source from (a) the metal sources, and (b) the substrate. This issue was resolved by putting reflector between the metal sources and the Se source and by adding another layer to the web shield. The double layer web shield made a substantial contribution in reducing the heat load, as evidenced by the steady state power usage, which went up to around 30% from 5% or lower. The Se effusion manifold was redesigned as a simple 3/8" diameter SS tube placed across the top of the sources in between the nozzles. The four holes on the tube are arranged so that two are between Cu-Ga and Ga-In sources, the other two are outside the Cu and In sources, respectively.

At the present time, the investigation centers around finding the minimum level of delivered Se without compromising Cu(GaIn)Se₂ film quality. The variables are a number of effusion holes i.e. center two or all four, hole diameter, and Se melt surface temperature. The results will be presented in the next report.

Wide Bandgap Materials

S-diffusion in Cu(InGa)Se₂

A Ph.D dissertation from the University of Delaware, Materials Science Department is titled "Surface Sulfurization of Copper Indium Diselenide for Application in Solar Cells" was completed by Jochen Titus. The dissertation abstract follows:

CuInSe₂-based chalcopyrite films can be used as absorber layers in thin-film solar cells. Some industrial manufacturing recipes of this type of solar cell involve a separate sulfurization step after absorber formation. The effects of this step on the absorber material, on its electronic properties and on device performance are only poorly understood. This project is part of a larger effort aimed at an understanding of the mass transport, the changes in material properties and the implications for device performance resulting from the application of this technique. For this project, the objective was an understanding of the mass transport taking place during the sulfurization of CuInSe₂ films, in particular the resulting distribution of S in the film, which replaces some of the Se in the chalcopyrite crystal lattice.

Samples were sulfurized in a flowing, H₂S-containing atmosphere, under conditions determined by annealing time and temperature and by gas composition and flow. Experiments were done on films as well as on single crystals. Samples were investigated with a range of analysis tools, most notably Auger electron spectroscopy (AES) depth profiling, X-ray diffraction (XRD), energy dispersive x-ray spectroscopy (EDS), scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Even subtle differences in sample-starting material were found to lead to vastly different modes of S incorporation. Rapid S incorporation was always correlated with a breakdown of the crystal lattice and with excess Cu. It occurred in films containing excess Cu, as well as in single crystals grown with the traveling heater method (THM) and with In as solvent. In these crystal samples, the excess Cu became apparent only after the sulfurization. A selenizing pre-anneal was effective in preventing the lattice breakdown in these crystals during sulfurization.

In single-phase film, as well as a vertical gradient freeze (VGF)-grown crystal, a slow S incorporation mode was active. There, the S distribution appeared to be the result of a fast chemical reaction at the solid-gas interface, which saturated the sample surface with S, and of subsequent solid-state interdiffusion of Se and S. In these samples the crystal structure was conserved during sulfurization. It was shown, that the S distribution in VGF crystals was the result of one-dimensional diffusion, governed by a concentration-dependent binary lattice diffusion coefficient D_1 , despite 4 elements (Cu, In, Se, S) being present. The value of D_1 was

determined, as a function of S concentration, with the help of the Boltzmann-Matano method from AES depth profiles.

The recording, of a meaningful AES depth profile on a sulfurized film, requires a film with a smooth front surface that must be conserved during sulfurization. After preliminary experiments on rough films, several attempts were made at preparing smooth films, since such films were not readily available. Chemo-mechanical polishing appeared to be the most promising method, but it still needs to be developed further, for experiments geared towards the determination of the values of both the lattice and the grain boundary diffusion coefficient in these films. For the evaluation of such experiments, a model of the interdiffusion in a film was implemented in the software FEMLAB.

Na-containing single-phase films behaved very similar to Na-free single-phase films. They also exhibited the slow S incorporation mode, but in addition, they segregated CuInS_2 and NaInS_2 on their free surface. The CuInS_2 was distributed evenly across the sample surface, but the NaInS_2 segregated in a particular pattern.

Fundamental Materials and Interface Characterization

Cu(InGa)Se₂ Optical Characterization

In the January 2004 report under this contract we showed the effect of Cu concentrations on the optical properties of Cu(InGa)Se_2 films, as measured by spectroscopic ellipsometry. In addition, the optical functions were used to calculate the volume fractions of different phases formed as a result of the Cu variation using both Bruggeman and Maxwell Garnet effective medium approximations (EMA). Since the optical constants also depend on the Ga/(In+Ga) ratio, the determination of the volume fractions of the different phases may be affected by the variation in the Ga ratio.

Hence a set of CuInSe_2 films was deposited by elemental co-evaporation to enable characterization of films, in which the optical properties are dependent only on the Cu ratio, $x \equiv \text{Cu/In}$. The composition of the films determined by EDS measurements are listed in Table 1 and shown relative to the $\text{CuSe}_2\text{-In}_2\text{Se}_3$ pseudo-binary phase diagram [1] in Figure 1. The films were deposited on Mo-coated soda lime glass substrates and then peeled using the method described elsewhere [2]. Ellipsometer measurements were performed immediately after peeling.

Table 1. Composition of the CuInSe_2 films used for the ellipsometry analysis.

Sample	Cu	In	Se	$x = \text{Cu/In}$
33485.21	25.2	25.6	49.3	1.00
33807.21	21.2	27.9	51.0	0.76
33808.21	18.2	30.0	51.9	0.61
33811.32	12.6	33.2	54.2	0.38
33817.32	11.3	34.4	54.3	0.33

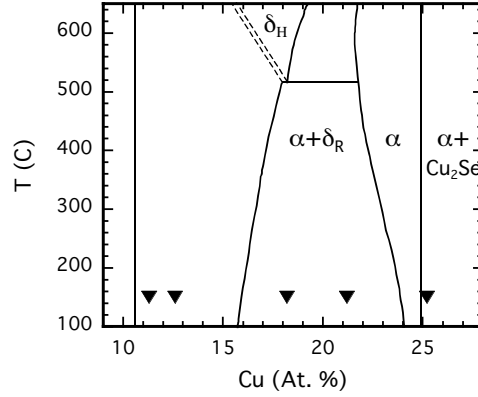


Figure 1. $\text{Cu}_2\text{Se-In}_2\text{Se}_3$ pseudo-binary phase diagram taken from Ref. 1. Triangles show the compositions of CuInSe_2 films used in this study.

The measured optical data, ϵ_1 and ϵ_2 , was modeled using the method described in the previous report. Optical constants for the single-phase $\alpha\text{-CuInSe}_2$ and $\delta_R\text{-Cu}_{0.33}\text{In}_{0.77}\text{Se}_2$ films are fit using oscillator levels in the optical models. The optical data in the two-phase $\alpha+\delta_R$ region was modeled using a Bruggeman effective medium approximation. The optical constants, thus obtained, are shown in Figures 2 and 3. These show a decrease in dielectric response and broadening of critical point features, with decreasing Cu ratio. This indicates that crystalline quality of the films deteriorated with decreasing Cu concentration.

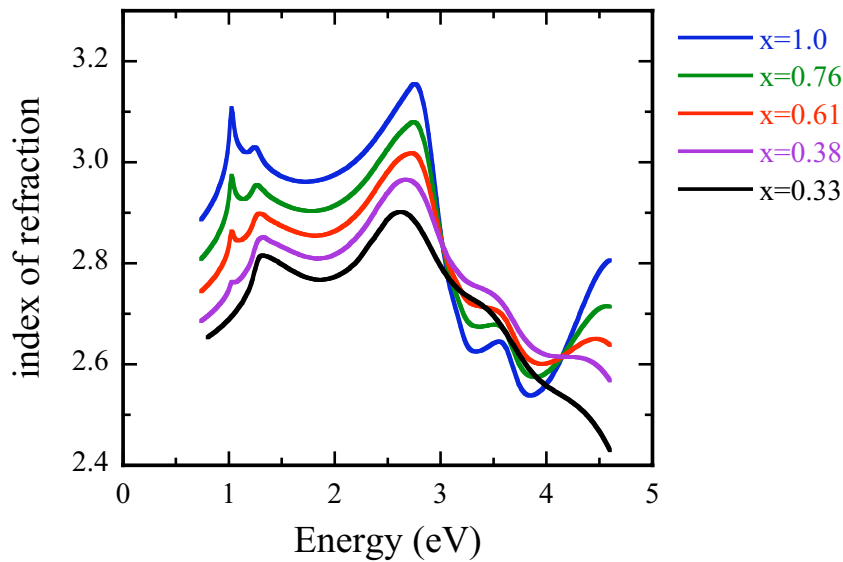


Figure 2. Index of refraction spectra for CuInSe_2 films obtained from the oscillator and EMA models.

Figure 3. Extinction coefficient spectra for CuInSe₂ films, obtained from the oscillator and EMA models

Mo/CuInSe₂ Interface Characterization

Characterization of the Mo/CuInSe₂-alloy interface is continuing. The goal is to determine the fundamental characteristics that control adhesion and affect device performance, focusing on the formation of a MoSe₂ interfacial layer during the CuInSe₂-alloy deposition. In the October 2003 report, under this contract, we reported characterization of the orientation of the MoSe₂ layer formed by reaction of Mo, Mo/Ga, and Mo/Cu layers in elemental Se at 450°C for 60 min. The films with the Cu layer, on either soda lime (SLG) or borosilicate (BSG) glass substrates, had a stronger relative (002) orientation than the selenized Mo or Mo/Ga layers. The MoSe₂ forms a layered structure and (002) orientation indicates planes with weak Se-Se bonds parallel to the substrate, which could cause poor adhesion.

Subsequent experiments were completed to characterize the MoSe₂ formation, in the presence of Al, since Cu(InAl)Se₂ films tend to have poor adhesion to Mo. In this case, Mo/Al/Cu layers were deposited to minimize oxidation of the Al. After Se reaction, Cu-Al intermetallic alloys were identified by XRD measurements but formation of MoSe₂ was negligible. Thus, this structure may not be suitable for characterization of the MoSe₂ growth and orientation with Al alloys. An alternative method is to peel the CuInSe₂-alloy film off of the substrate using epoxy. With Cu(InGa)Se₂ films, this was found to cleanly separate the Cu(InGa)Se₂ from the Mo with no Mo detected on the backside of the Cu(InGa)Se₂ film [2].

Figure 4 shows a symmetric θ -2 θ XRD scan of the Mo/MoSe₂ remaining on the substrate after peeling a Cu(InGa)Se₂ film. The Cu(InGa)Se₂ in this case was deposited by elemental evaporation at 550°C. The peaks identified by number in Figure 4 are listed in Table 1 and indexed as either Mo, MoSe₂, or Cu(InGa)Se₂. Thus, there is some residual Cu(InGa)Se₂ on the substrate. The MoSe₂ is oriented in the (002) direction indicating Se-Se layers parallel to the substrate.

This technique of characterizing the MoSe₂ growth after deposition and peeling of CuInSe₂-alloy films will be used to compare CuInSe₂, Cu(InGa)Se₂, and Cu(InAl)Se₂ films deposited on SLG and BSG substrates and also correlated to adhesion.

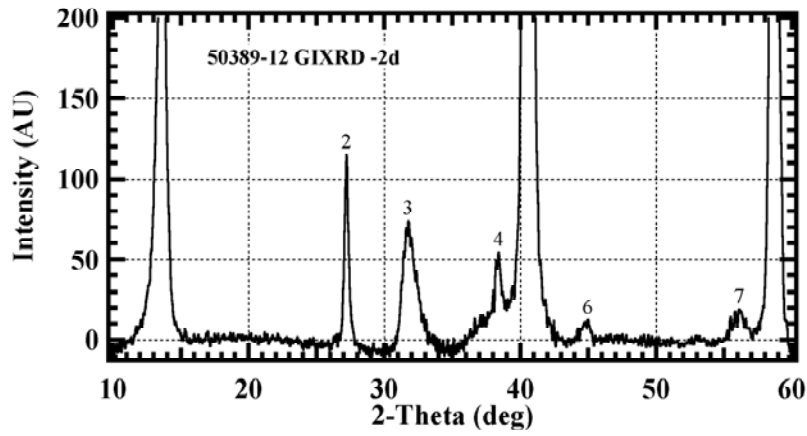


Figure 4. XRD scan of the glass/Mo substrate after a Cu(InGa)Se_2 film was peeled from it. The peaks are identified in Table 1.

Table 1. Identification of peaks in Figure 4 by comparison to JCPDS card files for Mo, MoSe_2 , and Cu(InGa)Se_2 .

No.	2- θ ($^\circ$)	Counts	d measured (\AA)	d (\AA) (hkl) for identified phase and JCPDS file		
				Mo(42-1120)	MoSe_2 (29-0914)	CIGS(35-1102)
1	13.64	293	6.486		6.46 (002)	
2	27.20	116	3.276			3.312 (112)
3	31.74	75	2.817		2.845 (100)	
4	38.40	55	2.342			
5	40.56	4332	2.222	2.2247 (110)		
6	44.96	13	2.014			2.028 (220/204)
7	56.10	20	1.638		1.643 (110)	
8	58.70	1480	1.571	1.5738 (200)		

Sincerely,

Robert W. Birkmire Director

RWB/bj

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Carolyn Lopez, NREL
Paula Newton
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References

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2. P.D. Paulson, R.W. Birkmire, W.N. Shafarman, J. Appl. Phys. **94**, 879 (2003).